

Dimethyl- and diethyldithiocyanato-  
tin(IV)

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The structures of dimethyldithiocyanatotin(IV),  $[\text{Sn}(\text{CH}_3)_2(\text{NCS})_2]$ , and diethyldithiocyanatotin(IV),  $[\text{Sn}(\text{C}_2\text{H}_5)_2(\text{NCS})_2]$ , have been determined. The dimethyl derivative has  $2mm$  crystallographic symmetry and the diethyl derivative has twofold crystallographic symmetry. The experimental differences in the distances and angles around the Sn atom between the two structures agree reasonably well with the differences expected from the reaction path mapped previously [Britton & Dunitz (1981). *J. Am. Chem. Soc.* **103**, 2971–2979].

## Comment

The path of the reaction  $R_2\text{Sn}X_2 + 2Y \rightarrow R_2\text{Sn}Y_2 + 2X$  was mapped (Britton & Dunitz, 1981; hereafter B&D) using the structure correlation method (Bürgi, 1975; Dunitz, 1975). A variety of  $R$  groups and  $X$  and  $Y$  atoms were used in this mapping, which showed rough but reasonable agreement for a variety of  $R_2\text{Sn}X_2Y_2$  intermediates. One of the compounds used in this study was  $(\text{CH}_3)_2\text{Sn}(\text{NCS})_2$  (Forder & Sheldrick, 1970; Chow, 1970). The availability of the corresponding diethyl compound suggested examining how the mapping changed with very small chemical differences.

In the structure of  $(\text{CH}_3)_2\text{Sn}(\text{NCS})_2$ ,  $\text{Sn}\cdots\text{S}$  interactions from adjacent molecules form partial bonds and lead to the weakening of the  $\text{Sn}-\text{N}$  bonds. A redetermination of this structure, (I), is reported here, along with the structure of  $(\text{C}_2\text{H}_5)_2\text{Sn}(\text{NCS})_2$ , (II). The replacement of methyl groups by ethyl groups must lead to a different overall packing arrangement, and the question of interest is the extent to which any changes in the  $\text{Sn}-\text{N}$  and  $\text{Sn}\cdots\text{S}$  distances and the  $\text{C}-\text{Sn}-\text{C}$ ,  $\text{C}-\text{Sn}-\text{X}$  and  $\text{C}-\text{Sn}\cdots\text{S}$  angles are consistent with each other and with the structure correlation model.

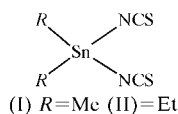


Fig. 1 shows the atom labeling and displacement ellipsoids for (I), along with a second molecule of (I) to make clear the  $\text{Sn}\cdots\text{S}$  interactions. Fig. 2 shows the same for (II). The bond

lengths and angles will be described below with one exception. In the B&D study it appeared that the  $\text{Sn}-\text{C}$  distances did not vary significantly from the  $\text{Sn}-\text{C}$  bond length of 2.10 Å given by Pauling (1960). In the present work, the  $\text{Sn}-\text{C}$  distance in (I) [2.099 (2) Å] is significantly smaller than that in (II) [2.126 (2) Å]. This discrepancy suggests that the original approach needs to be fine-tuned, but this difference has been ignored in the rest of the discussion.

The bond distances and angles are given in Tables 1 and 2. The  $\text{Sn}-\text{N}$  distance increases by 0.022 (2) Å from (I) to (II). The B&D model would predict that the  $\text{Sn}\cdots\text{S}$  distance should decrease, the  $\text{C}-\text{Sn}-\text{C}$  angle should increase, the  $\text{C}-\text{Sn}-\text{N}$  angle should decrease and the  $\text{C}-\text{Sn}\cdots\text{S}$  angle should increase. All of these qualitative changes are correct.

Using Pauling's (1947) bond length–bond order relationship [ $d(n) - d(1) = c \log n$ , with  $c = 1.20$  as used previously (B&D)], the bond orders,  $n$ , are those given in Table 1. They do not add to 1.000 owing to the approximate nature of the model. The sums of the  $n$  values could be brought closer to 1.000 by adjusting  $c$  slightly, but this does not seem justified.

In Table 2, the experimental  $\text{C}-\text{Sn}-\text{C}$ ,  $\text{C}-\text{Sn}-\text{N}$  and  $\text{C}-\text{Sn}\cdots\text{S}$  values are compared with the values predicted from the model of B&D. There are two sets of predicted values

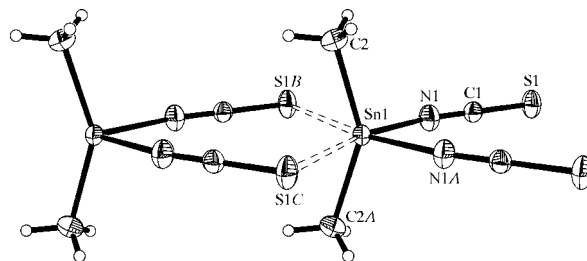


Figure 1

The crystallographically independent atoms in this view of the structure of (I) are labeled together with those additional atoms referred to in Tables 1 and 2. The molecule has  $2mm$  symmetry, with the twofold axis along  $[\frac{1}{4}, \frac{1}{4}, z]$ . Displacement ellipsoids are shown at the 50% probability level. The H-atom  $U_{\text{iso}}$  values were refined, but they are shown with arbitrary radii. The  $\text{Sn}\cdots\text{S}$  interactions are shown with dashed bonds. [Symmetry codes: (A)  $\frac{1}{2} - x, \frac{1}{2} - y, z$ ; (B)  $x, y, 1 + z$ ; (C)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 + z$ .]

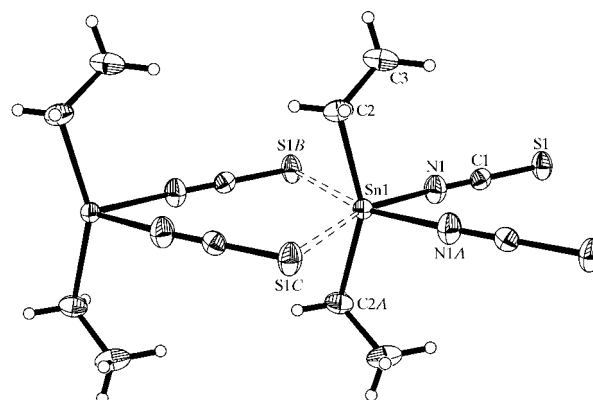


Figure 2

The molecule of (II) has 2 symmetry, with the twofold axis along  $[0, y, \frac{3}{4}]$ . All conventions are as in Fig. 1. [Symmetry codes: (A)  $-x, y, \frac{3}{2} - z$ ; (B)  $-x, 1 + y, \frac{3}{2} - z$ ; (C)  $x, 1 + y, z$ .]

depending on whether the C–N or C··S bond orders are used; in a perfect model these would be the same. The predicted values are in reasonable agreement with the experimental values, being within about 2°; the changes in going from (I) to (II) are within about 0.5° in all three cases.

## Experimental

The synthesis of (I) was described by Chow (1970). The synthesis of (II) was similar, with diethyltin chloride replacing dimethyltin chloride as the starting material.

### Compound (I)

#### Crystal data

[Sn(CH<sub>3</sub>)<sub>2</sub>(NCS)<sub>2</sub>]  
*M<sub>r</sub>* = 264.92  
 Orthorhombic, *Pmmn*  
*a* = 9.654 (2) Å  
*b* = 7.769 (2) Å  
*c* = 5.5692 (14) Å  
*V* = 417.70 (17) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 2.106 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 3997 reflections  
 $\theta$  = 2.6–27.5°  
 $\mu$  = 3.48 mm<sup>-1</sup>  
*T* = 174 (2) K  
 Needle, colorless  
 0.50 × 0.10 × 0.10 mm

#### Data collection

Siemens SMART area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996; Blessing, 1995)  
*T<sub>min</sub>* = 0.50, *T<sub>max</sub>* = 0.71  
 4698 measured reflections

543 independent reflections  
 523 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.018  
 $\theta_{\max}$  = 27.5°  
*h* = -12 → 12  
*k* = -9 → 10  
*l* = -7 → 7

#### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.009  
*wR* (*F*<sup>2</sup>) = 0.022  
*S* = 1.11  
 543 reflections  
 37 parameters  
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.011P)^2 + 0.108P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.23 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.19 \text{ e } \text{Å}^{-3}$   
 Extinction correction: *SHELXTL*  
 Extinction coefficient: 0.018 (3)

**Table 1**

Distances (Å) and bond orders<sup>a</sup>.

Bond	<i>d</i> (I)	<i>d</i> (II)	<i>n</i> (I)	<i>n</i> (II)
Sn1–N1	2.130 (2)	2.152 (1)	0.750 (3)	0.719 (2)
Sn1–S1 <i>B</i>	3.146 (1)	3.060 (1)	0.230 (1)	0.271 (1)

Notes: (a) The bond orders, following B&D, are based on the difference between the observed bond lengths and the Pauling (1960) single-bond distances: Sn–N = 1.98 Å and Sn–S = 2.38 Å.

### Compound (II)

#### Crystal data

[Sn(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>(NCS)<sub>2</sub>]  
*M<sub>r</sub>* = 292.97  
 Orthorhombic, *Pbcn*  
*a* = 14.449 (4) Å  
*b* = 5.5526 (14) Å  
*c* = 12.660 (3) Å  
*V* = 1015.7 (5) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.916 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 2765 reflections  
 $\theta$  = 3.2–27.4°  
 $\mu$  = 2.88 mm<sup>-1</sup>  
*T* = 174 (2) K  
 Plate, colorless  
 0.35 × 0.25 × 0.05 mm

#### Data collection

Siemens SMART area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996; Blessing, 1995)  
*T<sub>min</sub>* = 0.40, *T<sub>max</sub>* = 0.87  
 10750 measured reflections

1166 independent reflections  
 1137 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.021  
 $\theta_{\max}$  = 27.5°  
*h* = -18 → 18  
*k* = -7 → 7  
*l* = -16 → 16

#### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.014  
*wR* (*F*<sup>2</sup>) = 0.033  
*S* = 1.16  
 1166 reflections  
 73 parameters  
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.013P)^2 + 0.49P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.39 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.24 \text{ e } \text{Å}^{-3}$   
 Extinction correction: *SHELXTL*  
 Extinction coefficient: 0.0014 (2)

**Table 2**

Bond angles (°) observed (obs) and calculated (c)<sup>a</sup>.

Angle	<i>I</i> <sub>obs</sub>	<i>II</i> <sub>obs</sub> <sup>b</sup>	<i>I</i> <sub>c</sub> (N)	<i>II</i> <sub>c</sub> (N)	<i>I</i> <sub>c</sub> (S)	<i>II</i> <sub>c</sub> (S)
C2–Sn1–C2 <i>A</i>	147.6 (1)	153.0 (1)	146.4	150.7	143.7	149.4
C2–Sn1–N1	101.8 (1)	102.0 (1)	–	–	–	–
C2–Sn1–N1 <i>A</i>	–	98.0 (1)	–	–	–	–
C2–Sn1–N1 <i>av</i>	101.8	100.0	100.4	98.8	99.6	98.4
C2–Sn1–S1 <i>B</i>	82.1 (1)	83.1 (1)	–	–	–	–
C2–Sn1–S1 <i>C</i>	–	84.0 (1)	–	–	–	–
C2–Sn1–S1 <i>av</i>	82.1	83.5	79.6	81.2	80.4	81.6

Notes: (a) The first set of calculated values are based on the Sn–N bond orders, the second on the Sn··S bond orders. (b) Because the N1–Sn1–N1*A* and S1*B*··Sn1··S1*C* planes differ from coplanarity by 3.6 (1)°, there are two sets of C–Sn–N and C–Sn··S angles; these are averaged for the comparison with the angles calculated from the bond orders.

The solution and refinement were straightforward. As a test of the data, the H-atom positions and isotropic displacement parameters were refined and reasonable values were obtained even in the presence of the Sn atom [C–H = 0.925 (19) and 0.94 (3) Å for (I), and C–H = 0.91 (2)–0.99 (2) Å for (II)].

For both compounds, data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Both compounds were prepared by Dr Y. M. Chow.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3002). Services for accessing these data are described at the back of the journal.

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